

Multiconfiguration SCF calculations on CH_2O_2 ,
an intermediate in the ozonolysis of ethylene

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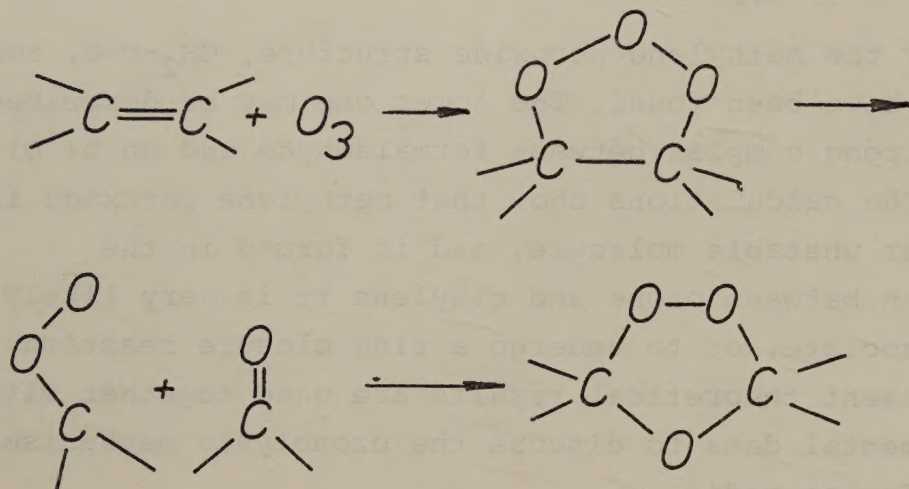
ABSTRACT

Multiconfigurational calculations, in a double zeta basis set augmented with polarisation functions, have been performed on the CH_2O_2 molecule, a proposed intermediate in the ozonolysis of ethylene. Extensive geometry optimization has been carried out and several minima and transition states have been located in the CH_2O_2 energy hypersurface.

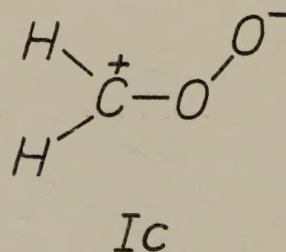
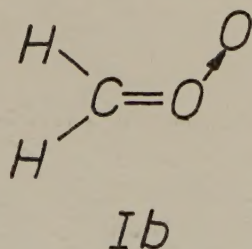
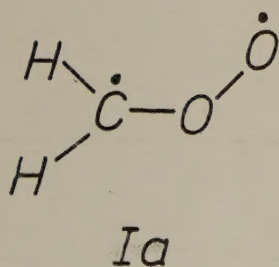
For the methylene peroxide structure, $\text{CH}_2\text{-O-O}$, two minima have been found. The lower one may be described as a strong complex between formaldehyde and an $\text{O}(^1\text{D})$ atom. The calculations show that methylene peroxide is a rather unstable molecule, and if formed in the reaction between ozone and ethylene it is very likely to dissociate, or to undergo a ring closure reaction. The present theoretical results are used together with experimental data to discuss the ozonolysis mechanism in different media.

INTRODUCTION

In 1949 Criegee and Weiner¹ proposed a mechanistic scheme for the reaction between ozone and olefins. This scheme was later extended², and its main features are now commonly accepted. Criegee suggested that ozone adds to the double bond in ethylene to form 1,2,3-trioxolane (primary ozonide). This molecule is reactive and dissociates into formaldehyde

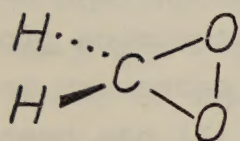


and methylene peroxide, which then recombine to give 1,2,4-trioxolane (secondary ozonide). Although the ozonolysis reaction has been extensively studied in different media, methylene peroxide has never been experimentally observed. The failure to observe methyleneperoxide is perhaps a weak point in the mechanistic scheme. Originally Criegee assumed methylene peroxide to be a zwitterion (Ic), however theoretical calculations

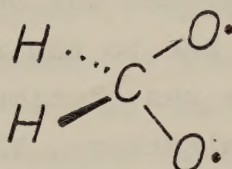


by Wadt and Goddard³ indicate a singlet biradical structure (Ia), analogues to O_3 . According to thermochemical studies by Benson⁴ methylene peroxide is best described as a complex between formaldehyde and an oxygen atom (Ib)

In order to obtain a better understanding of the reaction between ozone and olefins we have undertaken a number of ab initio multiconfiguration self-consistent field (MCSCF) calculations on methylene peroxide and the related compounds dioxirane (II) and dioxymethane (III). Some



II



III

aspects of the interconversion and decomposition of these three molecules have also been studied.

COMPUTATIONAL DETAILS

Several recent theoretical calculations on the ozone molecule have conclusively shown that the Hartree-Fock (HF) description of this molecule is inadequate⁵⁻¹¹, it has been further demonstrated that not even an HF-calculation followed by a configuration interaction (CI) calculation including all single and double replacement states is sufficient to obtain a good description of O_3 ¹¹. In addition it is well known that a single determinant calculation is incapable of describing a symmetry forbidden reaction. Such systems must be described by a wavefunction consisting of several determinants.

It is shown in the ozone calculations referred to above that a basis set of double zeta plus polarization functions quality is needed to obtain an accurate result. The basis set used in this work consisted of 9 s, 5 p and 1 d primitive functions on carbon and oxygen and 5 s on hydrogen¹² contracted to 4 s, 2 p, 1 d and 3 s respectively. The basis set has been contracted so as to obtain maximum flexibility in the valence region, rather than obtaining a low energy.

Our MCSCF-wavefunction consisted of ten closed shell configurations (see Table IIa-b). Calculations on the subsystems of CH_2O_2 was done in such a way that the combined system was described by a ten-determinant wavefunction. Due to the rather time-consuming procedure required, some restrictions have been necessary in the geometry optimizations. The structure (I) has been kept planar and the C-H distance and the H-C-H angle have not been optimized. Dioxirane (II) and dioxymethane (III) have been assumed to have C_{2v} symmetry. The energy minima in respective structures were located by fitting a full polynomial of second degree to the calculated energy values and finding the minimum thereof. The transition states were found as stationary points in the energy surface, with a Hessian matrix containing one negative eigenvalue.

All calculations were performed with the program system MOLECULE¹³.

RESULTS

A. Molecular Geometries

The calculated geometries for the different forms (I-III) of CH_2O_2 are shown in Figure I. The two methylene peroxide structures (Ia-b) in Figure I correspond to two distinct minima in the calculated energy hypersurface: the first having singlet biradical character, while the second may

be described as a complex between a formaldehyde molecule and an $O(^1D)$ atom. Table I contains the calculated total energies, from which it is seen that the energy difference between the two forms is only 27 kJ/mol, the complex-like structure being the lower. The coefficients and orbital occupancies of the determinants used in the MCSCF-wavefunction are presented in Table IIa. The singlet biradical character in structure Ia is shown by the fairly large coefficient for the second determinant. Population analysis of the different forms of CH_2O_2 , together with that of O_3 , calculated with the same basis set, is found in Table III. Two interesting observations can be made: firstly the difference in charge on the CH_2 -groups between the two forms of methylene peroxide, secondly the $O-O$ - overlap population which is negative but close to zero, in structure Ib as well as structure II. Differences between the results of the present work and those of previous investigations arise either from a more restricted basis set and lack of geometry optimization³, or from the use of a less sophisticated computational scheme^{14,15}.

Dioxirane (II) has recently been observed experimentally among the reaction products of the ozonolysis of ethylene^{16,17} and the $O-O$ - distance has been determined as 1.52 Å by microwave spectroscopy¹⁶. The difference between experiment and our calculated value of 1.60 Å, may be explained by the very shallow potential well for this coordinate. Thus the force constant for the $O-O$ bond is only 1/10 that of the $C-O$ bond. This means that the $O-O$ distance is difficult to determine by calculation since even small changes in the number of basis functions or determinants may drastically alter the result. The result may also be affected by vibrational averaging.

Although the calculated geometries may in some cases be somewhat uncertain, the calculated energies will be more reliable, since even fairly large errors in those geometry

parameters which have small force constants yield only minor contributions to the calculated total energy.

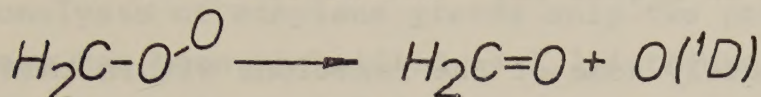
Dioxymethane (III) has not been observed experimentally. In this case, however, the calculated force constants give reason to believe that the calculated geometry is more reliable than the previous ones. One interesting feature in Figure 1 is the longer C-H bond in dioxirane compared to dioxymethane. The reason is that the $2b_2$ orbital, which is partly C-H binding, is missing in the leading determinant for dioxymethane. The almost equal coefficient for the two most important determinants in dioxymethane indicate that the triplet state is very close in energy to the singlet and might be the more stable state. The O_1-O_2 bond in ozone changes by 0.11 Å when going from the cyclic to the open form¹¹. The analogous change in the C- O_1 bond in the transformation from dioxirane to dioxymethane is only 0.012 Å. This is a reflection of the larger coefficient for the second determinant in dioxymethane (-0.63) as compared to ozone (-0.45). This determinant is antibonding in the C- O_1 and O_1-O_2 π -bond respectively. In the cyclic forms the π -orbitals contain six electrons, which does not contribute to the binding of the ring atoms.

B. Chemical transformations in the CH_2O_2 system

In the three-dimensional (i.e. subject to the above restrictions) energy surface of methylene peroxide a transition state was located between the two forms Ia and Ib. The geometry for the transition state is shown in Figure 2. The energy at this point is only 6.7 kJ/mole above that of the singlet biradical form (see Figure 3a). Such a small barrier makes it somewhat doubtful whether the singlet biradical minimum exists. A different choice of determinants or basis set may well destroy this minimum. Nevertheless the energy barrier of 6.7 kJ/mole is of the

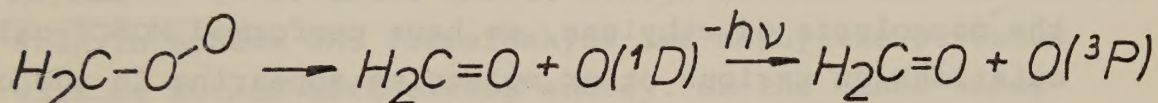
same magnitude as the zero-point vibration energy of an 0-0 stretching vibration making the form Ia most unstable.

For the dissociation



no saddle point was located. The reaction was found to be endothermic by 75.6 kJ/mol. This is twice the value calculated by Wadt and Goddard³ for the same process. Most of the difference is due to the lack of geometry optimization in their calculation.

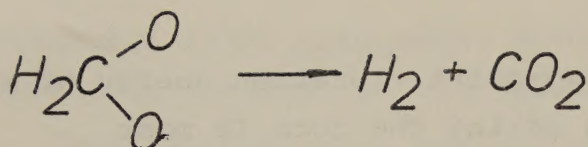
It is interesting to consider the reactions



to some extent. The overall process is exothermic by 114 kJ/mol since $\text{O}(^3\text{P})$ is 190 kJ/mol below $\text{O}(^1\text{D})$ in energy¹⁸. When the entropy contribution is taken into account the poor stability of methylene peroxide is clearly seen.

The two molecules dioxirane(II) and dioxymethane (III) have almost the same energy, the structure II being 6.9 kJ/mol more stable. From CI-calculations on O_3^{II} we estimate the effect of dynamical correlation to be less than 10 kJ/mol. The energy barrier for the transformation of dioxirane to dioxymethane was calculated to be 63.6 kJ/mol (see Figure 3b), thus at room temperature there exists a equilibrium between the two forms, 10^{-3} s being a characteristic time.

The calculated energy barrier, 125 kJ/mol for the reaction



is also shown in Figure 3b.

Unfortunately some of the reactions within this system, i.e. formation of dioxirane from methylene peroxide, formation of formic acid and perhaps also the formation of water and carbon monoxide from methyleneperoxide, occur via transition states with low or no symmetry making accurate calculations more expensive to perform.

C. Thermochemistry of the ozonolysis

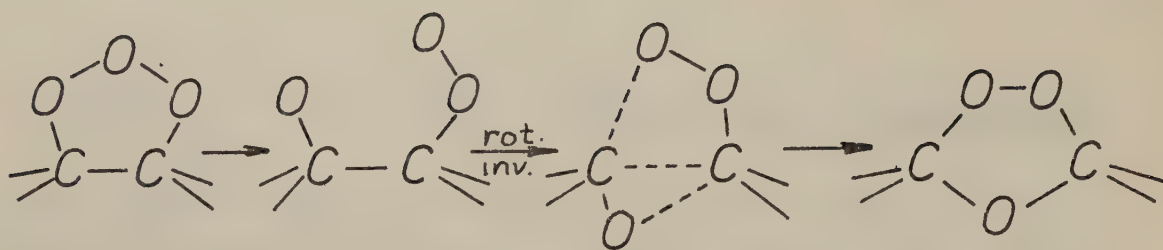
In order to get a good thermochemical description of the ozonolysis of ethylene, we have performed MCSCF-calculations on various other molecules appearing in the ozonolysis. These molecules and their total energies are listed in Table IV. From these results, the calculated energies of 1,2,3-trioxolane and 1,2,4-trioxolane of Wadt and Goddard³, and the use of standard heat of formation data for H₂O and CO¹⁹ a thermochemical scheme for the ozonolysis of ethylene has been constructed (Figure 4).

DISCUSSION

For the sake of clarity the discussion of the mechanistic implications from the present calculations is divided into three sections: The first section dealing with the ozonolysis reaction in a solid matrix, the second with the gas-phase reaction and the third with ozonolysis in the liquid phase. The reaction mechanism is assumed to be essentially the same in all media, however, the properties of the medium will determine the final product spectrum.

A. Reactions in solid matrix

In a recent IR study Nelander and Nord²⁰ showed that at low temperatures (77-90 K), in a matrix of CO₂ or CCl₄, ozonolysis of ethylene yields only two products. One of these has been identified as 1,2,4-trioxolane and the other seems to be 1,2,3-trioxolane. It can be concluded from isotopic labelling experiments^{21,22}, that 1,2,4-trioxolane is not formed from formaldehyde and dioxirane or dioxymethane; according to our thermochemical scheme this is not even thermodynamically possible (see Figure 4). This leaves at least two possible reaction pathways for the matrix reaction (see Scheme IA-B). The first step is the same in both ways with an activation energy of 10-20 kJ/mol^{20,23}. If there exists a high barrier for the second step in Scheme IB, formaldehyde and methylene peroxide will be formed with excess energy. On the other hand, if the barrier is low, the two molecules will be formed before the newly formed 1,2,3-trioxolane has been able to thermally relax and will thus contain excess vibrational and translational energy (see Figure 4). In both cases, however, it seems likely that the hot methylene peroxide will react further to form dioxirane, or formaldehyde and an oxygen atom. The barrier for the formation of dioxirane from methylene peroxide should be of the same order of magnitude as the barrier for the dioxymethane-dioxirane reaction (57 kJ/mol). In the matrix experiments of Nelander and Nord neither formaldehyde nor reaction products of O(¹D) were observed, and thus less than 5% of the reacting ethylene molecules produced one formaldehyde molecule²⁴. Consequently Scheme IB cannot be a major pathway in a low temperature matrix. The second step in Scheme IA is easily visualized in the following sequence



The first step in the above sequence has been considered by Hiberty and Devidal²⁵, who have calculated a barrier of 41 kJ/mol and an endothermicity of 28 kJ/mol for the ring opening reaction. The second intermediate in the sequence may be obtained either by rotation or inversion determining the stereostructure of the final product.

B. Gas-phase reaction

The main differences between matrix and gas phase ozonolysis are the lower capability of the surroundings to accept vibrational and translational energy from the reactive products and the entropy contribution to the free energy in the gas phase. The first mechanism will favour reaction products with high activation energy. The second factor will increase the formation of small molecules. Since the cooling of the reaction intermediates in the gas-phase is very slow almost all reaction pathways are possible. It might be worthwhile to point out that ethylene and ozone contain approximately 700 kJ/mol more energy than formaldehyde and formic acid. This makes it very difficult to give a mechanistic explanation covering all reaction possibilities. Many mechanistic proposals have been made^{3,14,16,26-29} and most of them may play a more or less important role in the actual reaction scheme.

In the mechanism given here (Scheme II) we merely wish to indicate what we suggest as the main reaction pathways. Scheme II explains all major reaction products observed in the gas phase ozonolysis of ethylene^{27,29}. The first two steps in the reaction scheme are similar to those of the matrix reaction. The third step is the dissociation

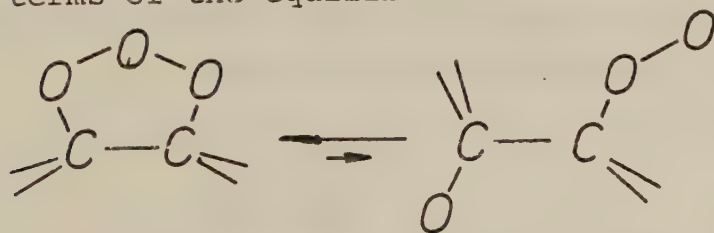
of the "complex" between formaldehyde and methylene peroxide. The fourth reaction occurs when the loosely bound oxygen atom abstracts the two hydrogens bound to the vicinal carbon atom. The activation energy for reactions 3 and 4 is probably larger than for reaction 5, but in the gas phase the slow cooling and the entropy contribution to the free energy favours reaction 3 and 4. Due to the poor cooling the secondary ozonide formed in step 5 dissociates into formaldehyde and dioxymethane. Dioxymethane may react further to give $\text{H}_2 + \text{CO}_2$ (step 8) and formic acid (step 9).

C. Reactions in the liquid phase

The main difference between matrix and liquid phase reactions is that translational motion enables product molecules to come together. This fundamental difference explains why 1,2,3-trioxolane is stable in matrices of CO_2 or CCl_4 at -100°C ²⁰ but not in liquid isobutane at -126°C ²³.

The 1,2,3-trioxolane molecule is probably stable in low temperature solutions with respect to unimolecular chemical reactions, however in the presence of high concentrations of other ozonides and polar molecules it will probably undergo dissociation or rearrangement reactions.

The mechanism for this process can be understood in terms of the equilibrium



in which the open form readily reacts with other polar molecules. The unimolecular part of the liquid phase reaction is similar to the gas phase reaction from a

mechanistic point of view. Due to the efficient cooling in solution the product distribution will of course be different.

CONCLUDING REMARKS

In the previous sections we have discussed only the ozonolysis of ethylene. However, many problems in the ozonolysis of olefins occur only for substituted species. The substituents on the olefins common in ozonolysis reactions are mainly of two types, either alkyl groups or fluorine atoms. The first type of substituent can easily be included in our mechanistic scheme, whereas fluorine atoms may drastically change the reaction scheme. Three different types of problems are usually discussed in relation to the ozonolysis of alkyl substituted ethylenes.

1. The stereospecificity of the reaction.
2. The incorporation of foreign aldehydes.
3. The formation of di- and polyperoxides.

The first point, the stereospecificity, is in our scheme explained by a substituent-dependent probability for rotation or inversion in Scheme A. The incorporation of foreign aldehydes occurs as described for the liquid phase reaction. The bulky alkyl substituents make steps 4,5,8,9,13 and 14 in Scheme II most unlikely due to steric hindrance. Consequently a large part of the reacting olefin leads to formation of a dioxirane analogue. The bulky substituents will favour the dioxirane analogue over the dioxyalkane. The dioxirane analogues formed may survive long enough to di- and polymerize as shown below



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FIGURE CAPTIONS

Figure 1. Calculated geometries for methylene peroxide (Ia-b), dioxirane (II) and dioxymethane (III). The C-H distance and the H-C-H angle were not varied but kept equal to 1.09 Å and 120° respectively for methyleneperoxide. All distances in Å units and angles in degrees.

Figure 2. Transition state for the transformation between the two states of methylene peroxide (a), dioxirane and dioxymethane (b) and for the dissociation of dioxymethane to hydrogen and carbon dioxide (c).

Figure 3a. Energy profile for the methylene peroxide system including formaldehyde and O(¹D). The energies are given in kJ/mol.

Figure 3b. Energy profile for part of the CH₂O₂ system. The energies are given in kJ/mol.

Figure 4. Thermochemical scheme for the ozonolysis of ethylene. All energies in kJ/mol. F = formaldehyde.

- a) Ref. 3.
- b) Ref. 18.
- c) Ref. 19.

Table I. Calculated total energies

	Energy (au)	Relative energy (kJ/mol)
Methylene peroxide (Ia)	-188.6004	144.5
Methylene peroxide (Ib)	-188.6107	117.4
Dioxirane (II)	-188.6554	0
Dioxymethane (III)	-188.6527	7.1

Table IIa. Coefficients for the determinants in the MCSCF-wave-function for the methylene peroxide like structures (Ia-b). Occupied orbitals outside the core, $1-9a_1^2$ are given.

	Determinants			Coefficients	
				(Ia)	(Ib)
1	$10a_1^2$	$1b_1^2$	$2b_1^2$	0.945	0.965
2	$10a_1^2$	$1b_1^2$	$3b_1^2$	-0.300	-0.198
3	$1b_1^2$	$2b_1^2$	$3b_1^2$	-0.004	-0.009
4	$11a_1^2$	$1b_1^2$	$2b_1^2$	-0.110	-0.163
5	$11a_1^2$	$1b_1^2$	$3b_1^2$	0.035	0.033
6	$10a_1^2$	$2b_1^2$	$3b_1^2$	0.063	-0.005
7	$10a_1^2$	$11a_1^2$	$1b_1^2$	-0.006	-0.004
8	$10a_1^2$	$11a_1^2$	$2b_1^2$	0.005	0.007
9	$10a_1^2$	$11a_1^2$	$3b_1^2$	-0.013	-0.035
10	$11a_1^2$	$2b_1^2$	$3b_1^2$	0.008	0.001

Table IIb. Coefficients for the determinants in the MCSCF-wavefunction for dioxirane (II) and dioxymethane (III). Occupied orbitals outside the core, $1-4a_1^2$ $1b_1^2$ $2b_1^2$ $1b_2^2$, are given

	Determinants	Coefficients	
		(II)	(III)
1	$5a_1^2 6a_1^2 3b_1^2 4b_1^2 1a_2^2$	-0.004	0.776
2	$5a_1^2 6a_1^2 3b_1^2 2b_2^2 1a_2^2$	0.958	0.001
3	$5a_1^2 6a_1^2 3b_1^2 4b_1^2 2b_2^2$	-0.034	-0.631
4	$6a_1^2 7a_1^2 3b_1^2 4b_1^2 1a_2^2$	0.000	-0.021
5	$5a_1^2 6a_1^2 4b_1^2 5b_1^2 1a_2^2$	0.000	-.041
6	$5a_1^2 6a_1^2 7a_1^2 4b_1^2 1a_2^2$	0.000	-.002
7	$5a_1^2 3b_1^2 4b_1^2 2b_2^2 1a_2^2$	-0.273	-.008
8	$5a_1^2 6a_1^2 4b_1^2 2b_2^2 1a_2^2$	-0.038	.001
9	$6a_1^2 7a_1^2 3b_1^2 2b_2^2 1a_2^2$	-0.058	.000
10	$6a_1^2 3b_1^2 5b_1^2 2b_2^2 1a_2^2$	-0.037	.000

Table III. Mulliken population analyses and dipole moments for different forms of the CH₂O₂ system^a

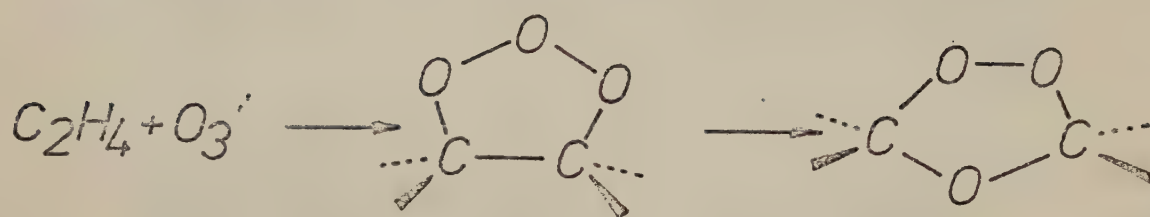
Molecule	Gross atomic population				Overlap population			Dipole moment	
	C	O ₁	O ₂	H ₁	H ₂	CO ₁	O ₁ O ₂	CH ₁	CH ₂ (D)
Methylene peroxide (Ia)	6.07	7.93	8.33	0.83	0.84	0.684	0.060	0.768	3.56
Methylene peroxide (Ib)	5.90	7.97	8.49	0.83	0.81	0.821	-0.007	0.726	5.61
Dioxirane (II)	5.69	8.25	8.25	0.90	0.90	0.458	-0.034	0.781	3.00
Dioxymethane (III)	5.78	8.26	8.26	0.85	0.85	0.456	-0.097	0.811	2.21
Ozone		7.90	8.05				0.082		

a)

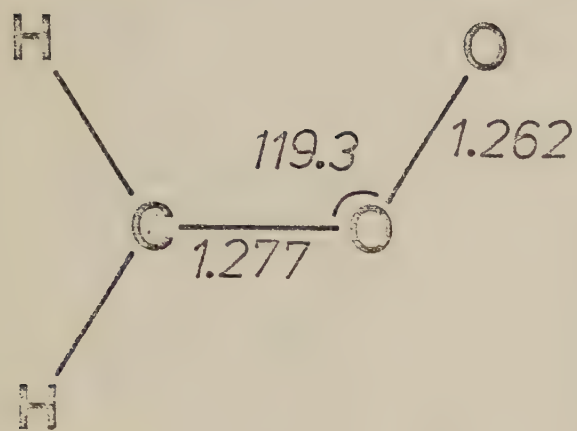
The numbering of the atoms refers to Figure 1

Table IV. Calculated total energies for some reactant and product molecules in the ozonolysis of ethylene

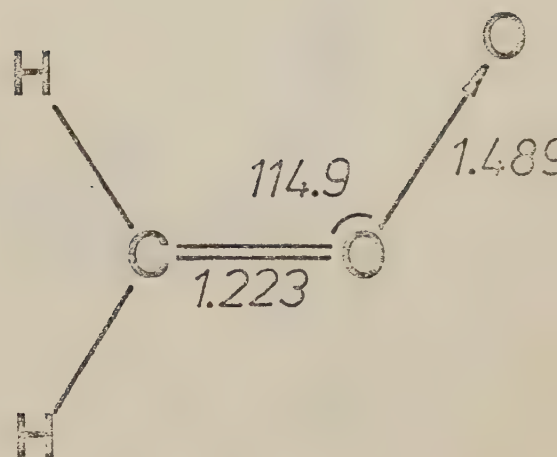
Molecule	Energies (a.u)	Number of determinants
C_2H_4	-78.0558	2
O_3	-224.3451	10
CH_2O	-113.8924	2
$O(^1D)$	-74.6895	3
CO_2	-187.6425	10
H_2	-1.1281	1
$HCOOH$	-188.7744	10



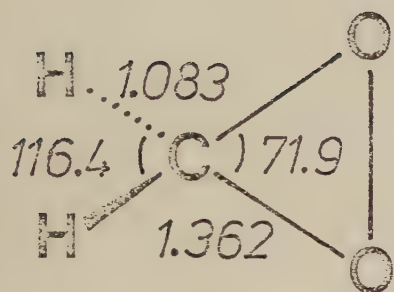
Scheme I



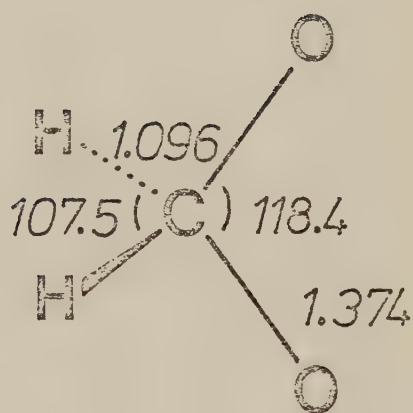
(Ia)



(Ib)

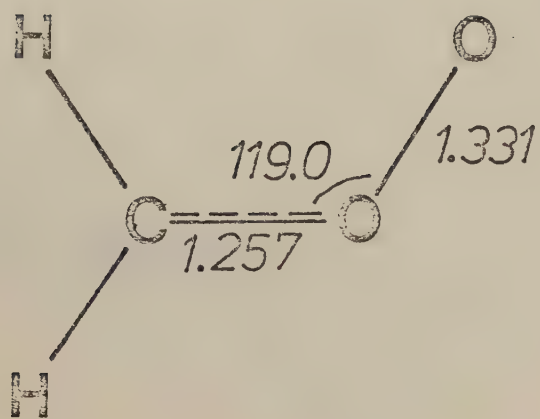


(II)



(III)

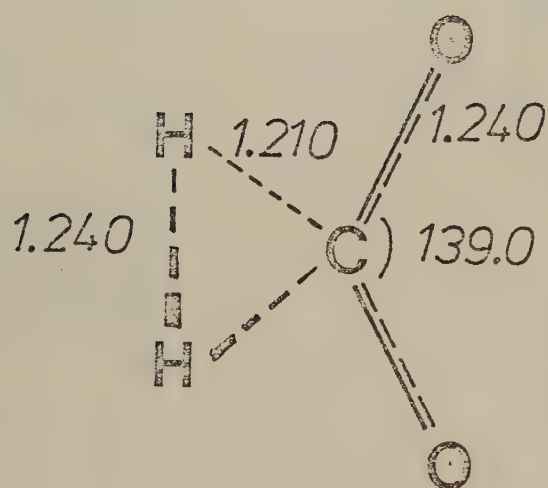
Figure 1



(a)



(b)



(c)

Figure 2

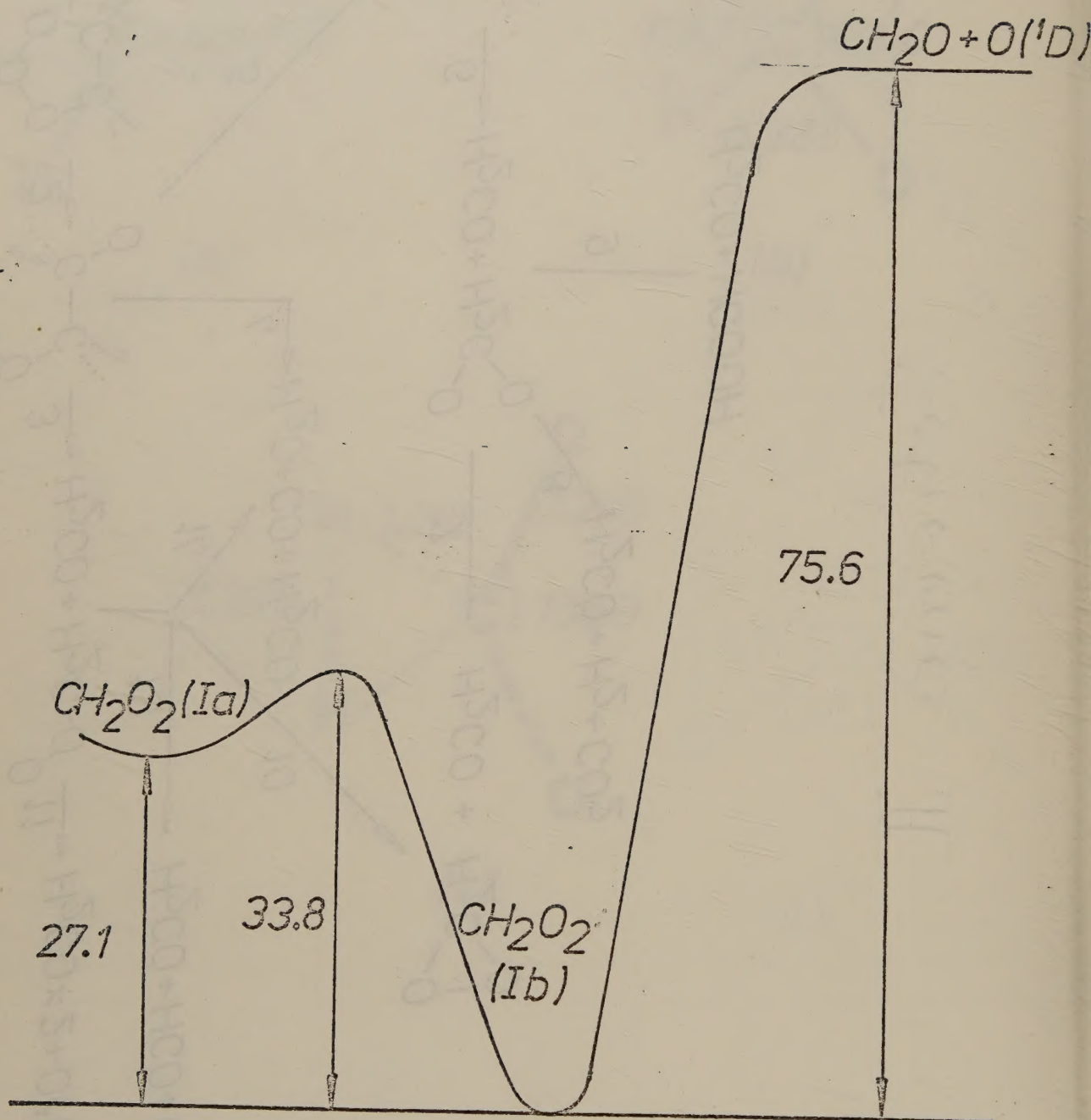


Figure 3a

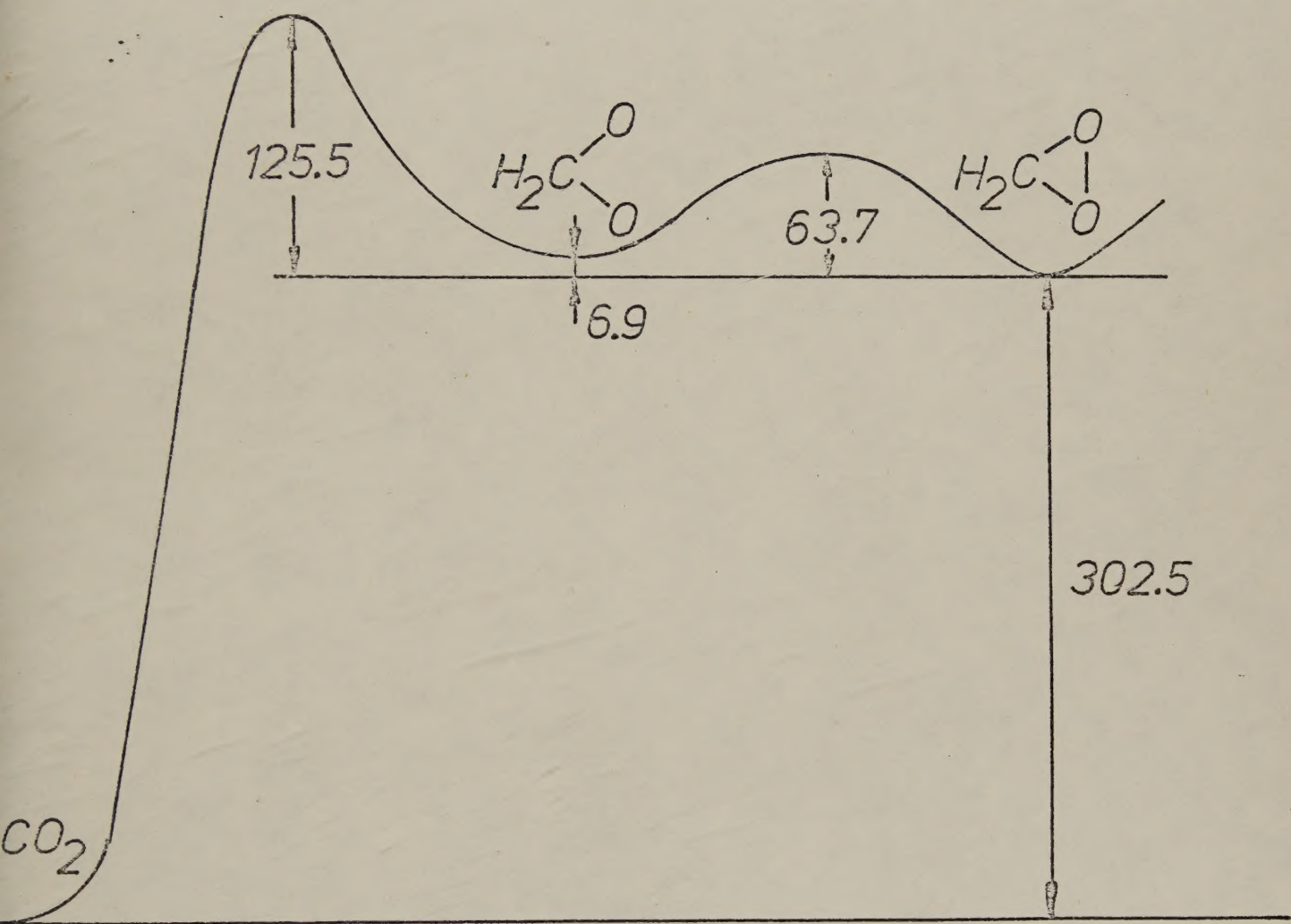


Figure 3b

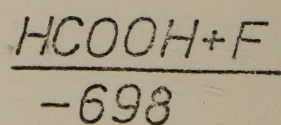
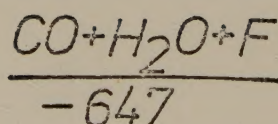
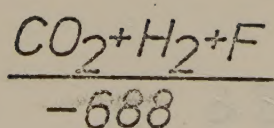
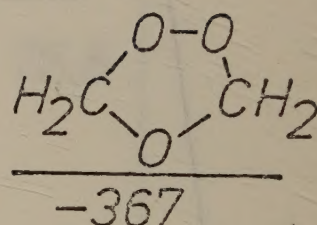
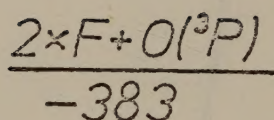
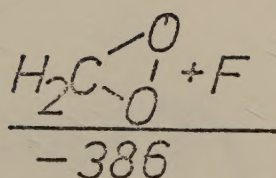
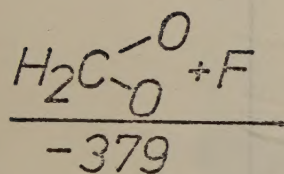
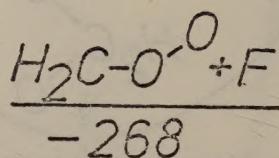
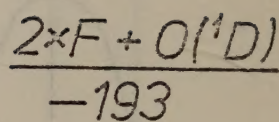
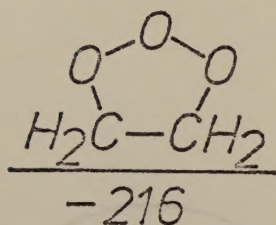
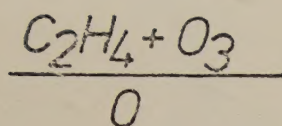


Figure 4